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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the carbon monoxide stripper in a fuel cell system, and the improvement art of the operating method.

[0002]

[Description of the Prior Art]A fuel cell system generates electricity by supplying the anode gas which contains hydrogen in the anode side of a fuel cell, and the cathode gas which contains oxygen in the cathode side, respectively, and making hydrogen and oxygen react electrochemically. Usually, although air is used as cathode gas, using lower alcohol, such as light hydrocarbon, such as natural gas naphtha, or methanol, as fuel as anode gas -- these -- reforming reactions, such as a steam reforming reaction or partial oxidation reaction, -- hydrogen -- what was made into rich reformed gas is used.

[0003]platinum (Pt) system currently used for the fuel cell system on the occasion of the reforming reaction of fuel -- the carbon monoxide (following CO) which carries out poisoning of the catalyst arises in a side reaction. By the time it reaches a fuel cell, about 1% of concentration will decrease in a CO transformer, but if CO stripper is added to this and this CO uses, it will become possible to reduce even the concentration below about 100 ppm (0.01%) of it (it indicates to JP,3-276577,A).

[0004]

[Problem(s) to be Solved by the Invention]By the way, in order to perform CO removal reaction (selective oxidation reaction), it is necessary to make the reformed gas introduced into CO stripper mix the gases (air etc.) which contain oxygen as an oxidizer beforehand. Here, near the gas inlet of CO stripper an oxygen density becomes comparatively high, a reaction reacts easily rapidly, if it goes up until catalyst layer temperature exceeds the appropriate temperature range with the reaction fever at this time, CO selectivity will fall and side reactions,

such as a combustion reaction of hydrogen harmful as a fuel cell system, will advance. Near the gas exhaust port of CO stripper, advance of the selective oxidation reaction which should be essentially performed by hypoxia contrary to a gas inlet will be barred.

[0005]On the other hand, to JP,8-47621,A or JP,8-133702,A, the air supply to CO stripper is adjusted according to the advance degree of a selective oxidation reaction, and the art of making a rapid advance of a reaction preventing is indicated, for example. However, if the amount of oxygen is reduced by regulation of this air content, the amount of oxygen for carrying out oxidation removal of CO may be insufficient, and it is thought that it also has the side effects that the selective oxidation reaction in the whole CO stripper is made to inhibit.

[0006]Now, it has the further hope about the technical development for raising the reaction efficiency of such a CO stripper. A rapid reaction [in / this invention is made in light of the above-mentioned problems, and / in the purpose / near the gas inlet of CO stripper], And it is in providing a CO stripper of the fuel cell system which can remove CO, and an operating method for the same, avoiding the problem relevant to temperature control, such as a reactant fall in near a gas exhaust port, and maintaining the efficiency of a selective oxidation reaction good.

[0007]

[Means for Solving the Problem]hydrogen in which this invention contains carbon monoxide in order to solve the above-mentioned problem -- air being mixed to rich reformed gas, and reactant gas being generated, and in a carbon monoxide stripper which removes carbon monoxide in said reactant gas according to a catalyst in a reactor, It was considered as a carbon monoxide stripper provided with a reactant gas dilution means which dilutes carbon monoxide and oxygen in reactant gas, making calorific capacity of reactant gas increase beforehand before carbon monoxide removal.

[0008]such a reactant gas dilution means -- oxygen/carbon monoxide (O_2/CO) -- without changing a ratio substantially, it becomes possible to control an excessive rise of reaction temperature, and efficient CO selective oxidation reaction can be performed. If a humidification means which humidifies air realizes said reactant gas dilution means, reactant gas can be safely diluted with a humidification means with a comparatively inertness steam added to air, and calorific capacity of the whole reactant gas is made to increase, and depressor effect of the above-mentioned rise in heat can be heightened.

[0009]Make a carbon monoxide stripper into a thing for fuel cell systems, and in humidifying air with cooling water of a fuel cell, said humidification means, It becomes unnecessary to more newly than the exterior have a device by exploiting resources in a system, and can contribute to miniaturization of a fuel cell system, and also becomes in cost and advantageous. If a carbon monoxide stripper is made into a thing for fuel cell systems and said reactant gas dilution means is equipped with a cathode exhaust gas feeding means which supplies cathode

exhaust gas of a fuel cell to the reformed gas side, Since it is the air where the amount of oxygen is reduced by operation of a fuel cell and which is in a humidified state, with the control effect of calorific capacity of reactant gas by the above-mentioned water. When O_2/CO is made equal compared with a case where the usual air is used, it can dilute with more steams and N_2 , and can be considered as a fuel cell system which performs a good selective oxidation reaction and from which electric power is obtained efficiently.

[0010]

[Embodiment of the Invention](Embodiment 1)

(Explanation of the entire configuration of a fuel cell system) Drawing 1 is a lineblock diagram of the solid polymer type fuel cell system concerning the embodiment of the invention 1.

[0011]Generate this fuel cell system using fuel gas, such as natural gas, town gas, and naphtha, and that composition made main, The desulfurizer 1 from which the sulfur component in fuel gas is removed, and the ejector 2 which mixes fuel gas with a hot steam, carrying out steam reforming of the fuel gas -- hydrogen -- with the reformer 3 which generates rich reformed gas. CO transformer 4 which oxidizes to CO_2 with a steam and removes CO in reformed gas (water gas shift reaction), The reformed gas from the CO stripper 5 which carries out selective oxidation of CO in reformed gas, and removes it further, and the CO stripper 5 is taken in to the fuel electrode (anode pole) 61, and it is roughly divided into the polymer electrolyte fuel cell 6 which takes in and generates the air which is an oxygen source to the air pole (cathode pole) 62.

[0012]The inside is filled up with a cobalt molybdenum (Co-Mo) system or a zinc oxide (ZnO) system catalyst for desulfurization in the desulfurizer 1, etc., Adsorption treatment of the various sulfur components, such as hydrogen sulfide (H_2S), an alkyl sulfide, etc. (R-SH) contained in fuel gas, is carried out by being heated to about 200 ** - near 300 ** with a heater (un-illustrating). by this embodiment, the refining method by a steam reforming reaction is used for the reformer 3 -- an inside -- as a reforming catalyst -- a nickel (nickel) system -- it comprises the cylindrical reformer 31 with which it filled up with the catalyst, and the burner 32 which burns fuel gas and carries out heating temperature up of said reformer 31 to an elevated temperature.

[0013]CO transformer 4, circulating the mixed gas of the reformed gas and the steam which the cylindrical cup is filled up with the copper-zinc system catalyst etc. as a catalyst for CO conversion, and are sent out from the reformer 3 in the pipe length direction. At the operating temperature of 180 ** - about 250 **, CO is oxidized to CO_2 (water gas shift reaction), and the CO concentration of reformed gas is reduced even to about 1% (10 or 000 ppm).

[0014]The CO stripper 5 comprises the selective oxidation reactor 51 and the air humidifier 56 at this embodiment. This selective oxidation reactor 51 and the air humidifier 56 of each other

are connected by the below-mentioned piping 52 and 105. Among these, the pipe length direction is carried out up and down, the cooling water A is filled till the middle of an inside, the cylindrical buffer tub 561 which makes the subject of the air humidifier 56 is blown into this cooling water A, and the air introduction pipe 55 is inserted via the buffer cistern cap 562 as a pipe. The humidified air flow conduit 54 is further inserted in the buffer cistern cap 562, and humidified air of the air part B of the cooling water A upper part is sent out by suction of the air pump 53 to the humidified air flow conduit 52. It is sent out to the piping 105 which sends reformed gas into the selective oxidation reactor 51, it is mixed with reformed gas, and generation of reactant gas is presented with the humidified air which flows through the humidified air flow conduit 52 concerned.

[0015]The refrigerant which circulates through the cooling water A through the annular piping 111 inside the cooling part 63 which it had as a cooling control part in the fuel cell 6 stagnates in the buffer tub 561. It is used for generation of said humidified air, the cooling water (about 80 **) with which the cooling process of fuel cell 6 inside was presented being supplemented with a lost part by evaporation etc. by a replenishing tank (un-illustrating), while once stagnating by said buffer tub 561 in this way. The cooling water A is introduced into the heat exchanger 112 by the drive of the pump 113 from the annular piping 111 after fixed time, and after being cooled to optimal temperature here, it is again sent into the cooling part 63.

[0016]As for the selective oxidation reactor 51, a cylindrical cup is filled up with a platinum-alumina ($\text{Pt-aluminum}_2\text{O}_3$) system catalyst etc. as a selective oxidation catalyst, Said reactant gas is incorporated into an inside, a selective oxidation reaction is performed in a catalyst appropriate temperature region (it is the range of about 100 ** - 250 ** in the case of the above-mentioned catalyst), and CO concentration is reduced below to about 0.01% (100 ppm).

[0017]The electrolyte part which the fuel cell 6 is a polymer electrolyte fuel cell, and was allotted between opposite of the anode (negative electrode) part 61, the cathode (anode) part 62 which counters this, and said polar zone 61 and 62 (un-illustrating), And it consists of cooling part 63 grade provided with said annular piping 111 inserted in the inside of fuel cell 6 case.

(Explanation about piping) As shown in drawing 1 as piping of a fuel gas (reformed gas) system, Fuel gas supply sources, such as town gas. From (un-illustrating), to the desulfurizer 1 fuel gas. From the desulfurizer 1, to the piping 100 and the ejector 2 to send fuel gas. The piping 101 to send, the piping 102 which sends fuel gas to the burner 32 of the reformer 3 from said fuel gas supply source, the piping 103 which sends the mixed gas of fuel gas and a hot water steam to the reformer 3 from the ejector 2, the piping 104 which sends reformed gas to CO transformer 4 from the reformer 3, From CO transformer 4, to the selective oxidation reactor 51 reformed gas. The piping 105 to send, the piping 106 and 108 which sends out

reformed gas to the anode part 61 of the fuel cell 6 through the cross valve 107 from the selective oxidation reactor 51, and piping which sends unreacted anode exhaust to burner 32 from anode part 61 109 grade are allocated.

[0018]As piping of a drainage system, the annular piping 111 which makes the cooling part 63 of the fuel cell 6, the air humidifier 56, and the heat exchanger 112 circulate through cooling water one by one is allocated. To the mixed gas (humidified air) of a steam and air, there are the humidified air flow conduits 54 and 52. Others are equipped with the bypass piping 110 as a gas stream Tooru course from the cross valve 107, in order to detour the fuel cell 6 and to send the piping 114 which sends air to the burner 32, and the gas sent out from the selective oxidation reactor 51 at the time of a system startup to the burner 32.

[0019]Although not illustrated for simplification of a figure, the valve (un-illustrating) which adjusts a flow is respectively inserted in these piping, and it can adjust according to the operation condition of a fuel cell system.

(Explanation about an operating method) In the starting early stages of this fuel cell system which has the above composition, in order to start the reforming reaction of fuel gas first, the temperature up of the reformer 31 of the reformer 3 becomes important. Therefore, a valve is operated so that all fuel gas may circulate the piping 102 and may be first sent to the burner 32 directly.

[0020]Next, air and fuel gas are sent into the burner 32 from the piping 114 and the piping 102, respectively, the burner 32 is lit, fuel gas is burned, and heating temperature up of the reformer 31 is carried out. The cross valve 107 is set up at this time circulate gas to the bypass piping 110 side. Heating temperature up also of CO transformer 4, the selective oxidation reactor 51, and the fuel cell 6 is simultaneously carried out with external heat, such as a heater (un-illustrating).

[0021]After heating temperature up of the reformer 31 is carried out to about 400 ** and temperature up of CO transformer 4 and the selective oxidation reactor 51 is carried out more than the dew point of a steam, a valve is operated, fuel gas is introduced into the desulfurizer 1, and desulfurization treatment is performed. Next, the fuel gas which carried out desulfurization treatment is introduced into the ejector 2 from the piping 101, and a hot steam is mixed with fuel gas here, and it introduces into the reformer 31 from the piping 103.

[0022]Next, the inside of the reformer 31 is made to pass said mixed gas, and a reforming reaction is made to start. Send the generated reformed gas to the CO transformer 4 and selective oxidation reactor 51 side one by one, it is made to circulate from the piping 106 to the piping 110, and the burner 32 is supplied. Thereby, heating temperature up of the reformer 31 is carried out to 700-800 ** of an operating temperature limit, and heating temperature up also of CO transformer 4 and the selective oxidation reactor 51 is carried out to CO conversion reaction by hot reformed gas, respectively.

[0023]When heating temperature up of the reformer 31, CO transformer 4, the selective oxidation reactor 51, and the fuel cell 6 is carried out to an operating temperature limit, the three way valve 107 is switched to the fuel cell 6 side, and operation is usually started. this -- the anode part 61 of the fuel cell 6 -- hydrogen -- since rich reformed gas is introduced and air is taken in by the cathode part 62 through the air pump 64 and the air introduction pipe 65, an electrochemical reaction advances and power generation is performed.

[0024>About 180-300 ** and the selective oxidation reactor 51 are about 100-250 **, and about 700-800 ** and CO transformer 4 is [the fuel cell 6 of the reformer 31 of the operating temperature limit of each composition in a fuel cell system] about 70-80 **. In this operating temperature limit, the electric power supply from the fuel cell 6 to external load is performed by this fuel cell system.

[0025]Usually, if the air humidifier 56 in the fuel cell system under operation is driven so that the air pump 53 may carry out the regurgitation in the humidified air flow conduit 52 direction, buffer tub 561 inside will be decompressed and the air of the fuel cell system circumference will be incorporated from the air introduction pipe 55 into the cooling water A in the buffer tub 561. This air is humidified as the dew point, moves the temperature (about 80 **) of the cooling water A to the air part B after that, and is sent out by the air pump 53 via the humidified air flow conduits 54 and 52 to the piping 105. The reactant gas which mixed the reformed gas and said humidified air mixed gas from CO transformer 4 is sent into the selective oxidation reactor 51 by this.

[0026]By the above composition, in order to avoid the extremes-of-temperature rise under selective oxidation reaction, the air of a reactant gas ingredient is humidified, but as a concrete operation from which the effect is acquired, the following two are mainly mentioned. That is, the depressor effect of the above-mentioned rise in heat is heightened by diluting the concentration of reactant gas ingredients, such as CO and O₂, using the volume of a steam, and increasing the calorific capacity of the whole reactant gas substantially using the calorific capacity of a steam.

[0027]This steam prevents desiccation of the electrolyte membrane (solid polyelectrolyte membrane) of a fuel cell, and in order to perform good power generation, it is used also for the purpose of carrying out humidity of the electrolyte membrane. In this embodiment, control is made so that the ratio of CO in reformed gas and O₂ in humidified air may be maintained with publicly known gas regulators, such as a valve. According to the presentation etc. of the fuel gas to be used, adjustment of setting out about this control is attained suitably.

[0028](Embodiment 2) The embodiment of the invention 2 is described continuously. Drawing 2 is a schematic diagram showing the main composition of the fuel cell system in this embodiment. Although many of system configurations are the same as that of Embodiment 1, the humidified air generated with the air humidifier 56 is used with the fuel cell 6, and it differs

in that what was made into cathode exhaust gas is introduced to the selective oxidation reactor 51 of the CO stripper 5.

[0029]Generally in the fuel cell, air is used as an oxygen source. the steam which the amount of oxygen decreased several percent from the beginning when the air supplied to a fuel cell was discharged, and the nitrogen volume to the amount of oxygen increased since the hydrogen ion reacted to oxygen in near a cathode and water arose in the acid electrolyte type fuel cell -- it becomes rich exhaust gas (cathode exhaust gas). Especially in a polymer electrolyte fuel cell, since humidified air is supplied to the cathode side in order to maintain an electrolyte membrane to a damp or wet condition, in cathode exhaust, comparatively many nitrogen and steams will be contained to oxygen. Since these [both] can make the calorific capacity of reactant gas increase, they use this cathode exhaust gas as a reactant gas ingredient in this embodiment.

[0030]As shown in drawing 2 as the concrete means, it has the cathode exhaust gas feed pipe 69 connected with the exhaust pipe 68 of the cathode part 62 the piping 105 side. The air pump 70 is arranged to the cathode exhaust gas feed pipe 69. The bypass piping 66 directly linked with the air introduction pipe 65 and said exhaust pipe 68 of the cathode part 62 is formed, and the cross valve 67 is allocated in the connecting part of the bypass piping 66 concerned and the air introduction pipe 65.

[0031]In this fuel cell system, in order to carry out humidity of the electrolyte membrane of the fuel cell 6, the air humidified with the air humidifier 56 is introduced to the cathode part 62. (Operating method of a fuel cell system) The operating method of the above fuel cell systems of composition is performed as follows with operation of a system. A part of explanation which overlaps with said embodiment is omitted.

[0032]The operation in early stages of [starting] the fuel cell system concerned is the same as that of the aforementioned system almost. Fuel gas is first sent into the burner 32 from the piping 102, this is burned, and heating temperature up of the reformer 31 is carried out to about 400 **. Then, fuel gas is sent to the desulfurizer 1 and reformer 31 side, and the cross valve 107 is adjusted so that the inside of CO transformer 4 and the selective oxidation reactor 51 may be circulated one by one and it may introduce into the burner 32 from the piping 110. The cross valve 67 is adjusted in parallel with this, and usual humidified air is sent into the piping 105 by the air pumps 64 and 70. After CO transformer 4 and the selective oxidation reactor 51 result after fixed time at the level of each reaction which can be started, Said cross valve 107 is operated, the reformed gas from the selective oxidation reactor 51 is circulated to the anode part 61 side of the fuel cell 6, the cross valve 67 is set to the cathode part 62 side, and humidified air is introduced to the cathode part 62. Thereby, power generation is started with the fuel cell 6, and cathode exhaust gas is introduced into the reactant gas to the selective oxidation reactor 51. The CO stripper 5 and a fuel cell system can be made to usually shift to

operation in the above operation.

[0033]The presentation of the reactant gas introduced into (explanation of reactant gas composition ratio and reaction efficiency), next the above-mentioned CO stripper of Embodiments 1 and 2 and the reaction efficiency of CO stripper are explained using the figure (drawing 3) showing reactant gas composition ratio, and the figures (drawing 4) showing the temperature distribution of the catalyst bed in the selective oxidation reactor 51. As fuel gas introduced into a fuel cell system, the town gas 13A (presentation; methane 88% and ethane 6% and propane 4% and butane 2%) was used. The mole fraction (steam/carbon ratio) of the water molecule of the steam introduced into the reformer in a reformer and the carbon atom in fuel gas is about 2.5. Near about 700 °C and the conversion reaction temperature in the CO transformer were set up near about 230 °C for the reforming reaction temperature in a reformer, respectively.

[0034]Mix various kinds of gases to the reformed gas 301 sent out to drawing 3 from CO transformer 4, and it is considered as reactant gas, The gas (conventional example) 302 which mixed the usual air, the gas (embodiment 1) 303 which mixed the air (80 °C of dew point) humidified by the cooling water of the fuel cell 6, and cathode exhaust gas of the fuel cell 6 (50% of an air utilization rate) The ingredient of the reactant gas of the gas (embodiment 2) 304 which mixed 80 °C of dew point was shown. He is trying to set O_2 / CO ratio to 3, respectively. Reaction gas composition consists of ingredients, such as H_2 , CO , CO_2 , CH_4 , H_2O , N_2 , and O_2 , among these CO and O_2 ingredient are mainly related to the selective oxidation reaction of CO (selective oxidation reaction; $CO + 1/2O_2 \rightarrow CO_2$).

[0035]The gas mass flow per 1 kW of cell outputs is as follows in each embodiment and a conventional example (in the case of 70% of hydrogen utilization, and the average cell voltage 0.6V).

Conventional example; 28.7 L/min embodiment 1; 31.0 L/min embodiment 2; So that clearly from the figure of 35.3 L/min °C, In the conventional air mixed gas 302, to H_2O being contained about 10.9%, if it results in the cathode exhaust air mixed gas 304 17.5%, in the humidified air mixed gas 303, it reaches to 20.6%. Thus, the reactant gas in the above-mentioned embodiment contains H_2O by twice [over the past / about] as many composition ratio as this. As for O_2 / CO ratio, since oxidation reaction of other ingredients arises with some with the selective oxidation reaction of CO , it is preferred to set up more (they are O_2 / CO ratio about three) amounts of O_2 than a theory top.

[0036]If the reactant gas of the above presentations is introduced into the selective oxidation reactor of CO stripper, the temperature distribution of an oxidation catalyst layer will become

as it is shown in the temperature distribution table of drawing 4, respectively. In this figure, the air mixed gas 302 of the former [(i) / curvilinear] and curvilinear (ii) show the humidified air mixed gas 303, and curvilinear (iii) shows each temperature curve of the cathode exhaust air mixed gas 304. When the about about 100-150 ** air mixed gas 302 is first introduced into selective oxidation reactor 51 inside, in order to react rapidly near a gas inlet soon after introduction, a catalyst bed carries out a rise in heat, and comes to reach a high temperature state (about 200-250 **). Since the maximum of the appropriate temperature field of a selective oxidation reaction is near about 200 **, after gas is introduced into a reactor, it will be restricted that CO removal is made by the time a catalyst bed arrives at this high temperature region. However, as curvilinear (i) showed, the field of the actual catalyst bed which can succeed in a selective oxidation reaction was restricted near [this] the gas inlet.

[0037]However, on the other hand, when the humidified air mixed gas 303 (curve ii) is introduced into a selective oxidation reactor (51), since O₂ ingredient is diluted even if reactant gas contacts a selective oxidation catalyst, a reaction is inhibited, and a reaction is started quietly. Since the calorific capacity of reactant gas is increasing by the increase in a steam and a rise in heat with rapid reaction temperature is also avoided, as shown in drawing 4, the ascending curve of catalyst temperature becomes loose, and the field of the catalyst bed which contributes to the part selective oxidation reaction becomes long ranging from the gas inlet to a gas outlet. Thereby, CO removal efficiency improves.

[0038]When the cathode exhaust 304 (curve iii) is used, in addition to the effect of the above-mentioned humidified air mixed gas 303 (curve ii), there is the following effect. Compared with air, the oxygen density of the cathode exhaust 304 usually by operation of a fuel cell Namely, since it is low, When the dew point, and O₂ / CO ratio are made to be the same as that of the humidified air mixed gas 303, N₂ in gas and a water vapor content will increase further, and the depressor effect of oxidation reaction improves by this. Since calorific capacity also increases, it can succeed in more effective control to the rise of reaction temperature.

[0039]Generally the effect is proportionally acquired by making the steam saturation content of reactant gas into the maximum by the range at the time of making the water vapor content of the air of the carbon monoxide stripper circumference into the minimum in the quantity of the steam which adds the effect by such a steam to reactant gas. In this range, the effect which dilutes carbon monoxide and an oxygen density and raises the efficiency of a selective oxidation reaction becomes high, making the calorific capacity of reactant gas increase so that there are many water vapor contents. However, since it needs the heat source for steam generating in adding a steam so much, it cannot be overemphasized that it is necessary to adjust an addition in consideration of the heat balance of a system. Although a water vapor content is slightly effective at least, since the direction which used exhaust heat of the fuel cell 6 and set up the addition by making the temperature (about 80 **) grade of cooling water or

cathode exhaust gas into the dew point does not newly need to be provided with the equipment for humidification and can obtain an effective result, it is desirable.

[0040] Although the embodiment showed the example which mixes a steam to reactant gas, since what is necessary is just a comparatively inertness ingredient, otherwise, it may be N_2 to the selective oxidation reaction of CO. However, when using N_2 etc., the equipment for supplying this must be allocated separately. Although the reactor 51 furthermore showed the example which is cylindrical shape by the above-mentioned embodiment, rectangular pipe shape etc. may be sufficient.

[0041]

[Effect of the Invention] the hydrogen in which this invention contains CO so that clearly from the above explanation -- air being mixed to rich reformed gas, and reactant gas being generated, and in the carbon monoxide stripper which removes CO in said reactant gas according to the catalyst in a reactor, Since it has a reactant gas dilution means which dilutes CO and oxygen in reactant gas, making the calorific capacity of reactant gas increase beforehand before CO removal, It is effective in becoming possible to remove CO, being able to avoid that a selective oxidation reaction advances rapidly near the gas inlet of a reactor like before, and reaction efficiency falls, and maintaining the efficiency of a selective oxidation reaction good.

[Translation done.]